Model Potential for Atoms and Ions

AUTHOR(S):

Mukoyama, Takeshi; Hock, Gábor

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 71, No. 1, 1993

Model Potential for Atoms and Ions

Takeshi MUKOYAMA* and Gábor HOCK†

Received February 9, 1993

A method to calculate the model potential for atoms and ions from the numerical potential has been developed. The method consists of the numerical calculation of the self-consistent-field potential taking into account all the electrons and the least-squares fitting of the numerical potential to an the appropriate analytical function. The sample calculations are performed in the case of neutral atoms and ions for the Hartree-Fock-Slater (HFS) potential. The results are tested by comparing energy eigenvalues and radiative transition probabilities with those obtained by the HFS potential.

KEY WORDS: Model potential/ Self-consistent-field potential/ Nonlinear least-squares method

1. INTRODUCTION

When there is a single electron in atoms or ions, the atomic potential is given analytically by a hydrogenic (or pure Coulomb) potential. Atomic energy levels and wave functions can be calculated easily for such a system. In the case of two-electron systems, the atomic Hamiltonian is expressed explicitly and theoretical models for accurate atomic states and wave functions are available. However, for many electron systems, i.e. atoms and ions with more than three electrons, simple atomic calculations are generally difficult and it is usual to use the Hartree-Fock (HF) approximation.

In the HF method, the energy and wave function for each electron are evaluated by solving the single-particle Schrödinger equation with the atomic potential determined self-consistently. The HF calculations of many electron systems have usually been performed with computers and the self-consistent-field (SCF) potential is obtained in numerical form.

On the other hand, there have been reported several attempts to describe atomic potentials for many electron systems in simple analytical functions. This approach, called the *model potential,* has beem used in atomic and molecular structure calculations,[1,2] coupled-channel calculations for ion-atom collisions,[3,4] and classical trajectory Monte Carlo (CTMC) method in atomic collisions.[5,6]

In atomic and molecular structures, the *model potential,* sometimes called *pseudopotential or optical potential,* is often used to describe the approximation that the contributions from the *core* electrons are expressed by an effective potential in which the *valence* electrons move and atomic or molecular properties are obtained by solving the Schrödinger equation only for the valence

* 向山 毅 : Division of States and Structures, Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611 Japan.

† Gábor HOCK : Institute of Nuclear Reserch of the Hungarian Academy of Sciences (ATOMKI), H-4001 Debrecen, PF. 51, Hungary.

electrons. This model potential method has been applied to calculate energy levels, oscillator strengths, life times, and photoionization cross sections.[1,2] However, in the present work we use this term, the *model potential,* in more generalized meaning, i.e. atomic potential given in terms of analytical functions.

Various forms of analytical functions and methods to adjust their parameters have been proposed.[1-7] In the present work, we develope a simple method to obtain the model potential by fitting the numerical SCF potential obtained in the HF approximation to an appropriate analytical function by the use of the nonlinear function minimization technique.

2. COMPUTATIONAL METHOD

For many-electron atoms or ions, the atomic potential is given in the numerical form by the HF method. This potential, $V(r)$, can be approximated by the analytical form

$$-rV(r)=a+b(1+c_1r+c_2r^2+\ldots+c_nr^n)\exp(-\mu r), \tag{1}$$

where r is the radial distance. This type of model potential was first proposed by Daniele[8] and used by Bransden *et al.*[3] in coupled-channel equations for ion-atom collisions and by Katsonis and Maynard[6] in the CTMC calculations.

In the present work, we calculate the numerical SCF potential with the Hartree-Fock-Slater (HFS) method by the use of the Herman-Skillman (HS) program.[9] The HFS method is one of the modifications of the HF method, where the exchange potential is approximated by the term proportional to one-third of the local charge density. In the HS program, the asymptotic behavior of the HFS potential at large r is modified by the Latter tail correction.[10] Considering this correction, the model potential in Eq. (1) satisfies the boundary conditions[9]

$$-rV(r)\to Z \text{ as } r\to 0, \tag{2}$$

$$-rV(r)\to Z-N+1 \text{ as } r\to\infty, \tag{3}$$

where Z is the atomic number, N is the number of electrons, and $(Z-N)$ corresponds to the degree of ionicity. From Eqs. (2) and (3), the paramenters a and b can be determined to be

$$a=Z-N+1, \tag{4}$$

and

$$b=N-1. \tag{5}$$

The polynomial in Eq. (1) is chosen up to $n=2$. The three parameters, c_1, c_2, and μ, are determined by fitting the numerical HFS potential to Eq. (1) with the nonlinear least-squares method. For this purpose, the nonlinear function minimization technique developed by Powell[11] is used.

3. RESULTS AND DISCUSSION

All the numerical computations in the present work have been perfomed on the FACOM M-760/10 computer in the Institute for Chemical Research, Kyoto University.

First, the HFS calculation for atoms and ions is made and the numerical SCF potential is

obtained. The HS program is used for this purpose, i.e. the Slater exchange parameter is taken to be $\alpha=1$ and Latter tail correction is included. Then the numerical potential is fitted to the analytical function in Eq. (1) by the nonlinear least-squares method. Starting from appropriate initial estimates for the parameters, c_1, c_2, and μ in Eq. (1), the parameter values are improved at each step of the iteration and the final values are determined when the convergence criteria are met.

The values of the parameters for Ne atom and ions are listed in Table I. It can be seen that all the parameters change smoothly as a function of the degree of ionicity up to Ne^{6+}, but there is a sudden jump at Ne^{7+}, the Li-like neon. In all cases, the model potential is in good agreement with the numerical HS potential. The discrepancy between two potentials is less than 1% everywhere except for several points.

In Fig. 1, The model potential for neutral neon atom obtained with the parameters in Table I, $-rV(r)$, is plotted against the radial distance from the nucleus, r, and compared with the numerical HS potential. For comparison, another model potential, proposed by Green, Sellin, and Zachor (GSZ),[7] is also shown in the figure. The GSZ potential was first developed for

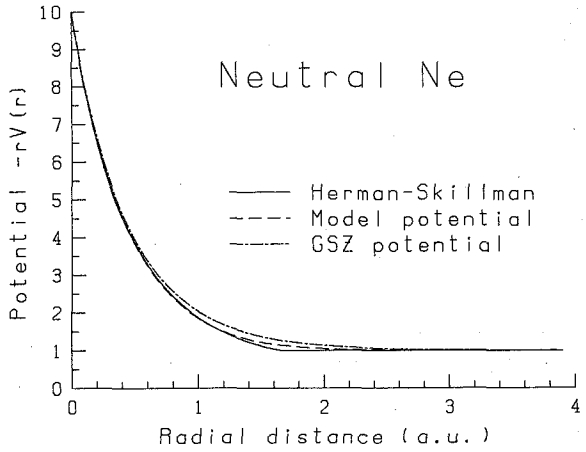

Fig. 1. Comparison of atomic potentials for neutral Ne.

Teble I. Values of the parameters for Ne.

	c_1	c_2	μ
Ne	1.1454	1.8629	3.7486
Ne^{1+}	1.3405	2.2355	4.1556
Ne^{2+}	1.4992	2.5733	4.5500
Ne^{3+}	1.5985	2.7115	4.9159
Ne^{4+}	1.6200	2.4282	5.2490
Ne^{5+}	1.5338	1.3226	5.5482
Ne^{6+}	2.4567	0.0004	6.9423
Ne^{7+}	3.2226	−13.0248	8.3644

Teble II. Values of the parameters for Ti.

	c_1	c_2	μ
Ti	−0.47031	2.0969	2.8453
Ti^{1+}	−0.26860	2.4763	3.2898
Ti^{2+}	−0.003647	2.9535	3.8044
Ti^{3+}	0.030691	3.0978	4.0366
Ti^{4+}	0.025159	3.1764	4.2263
Ti^{5+}	−0.026415	3.1345	4.3866
Ti^{6+}	−0.078240	3.0545	4.5574
Ti^{7+}	−0.11249	2.9348	4.7723
Ti^{8+}	−0.082007	2.7790	5.0870
Ti^{9+}	0.16515	2.6671	5.6675
Ti^{10+}	1.0816	3.3153	6.9836
Ti^{11+}	−0.78184	−0.0000	5.3448

neutral atoms and then generalized to ions. The generalized GSZ potential has a form

$$-rV(r)=(Z-1)\Omega(r)+1, \tag{6}$$

$$\Omega(r)=[H(e^{r/d}-1)+1]^{-1}, \tag{7}$$

where H and d are adjustable parameters. The parameter H is expressed as

$$H=d(Z-\eta)^{0.4}, \tag{8}$$

where η is the degree of ionicity plus one. The parameter d is tabulated in their paper for elements between Z=3 and 103.[7] In the case of Ne, d is equal to 0.500.

It can be seen in Fig. 1 that two model potentials are in good agreement with the HS potential, but in the region where the slope of the potential changes rapidly both model potentials

Teble III. Values of the parameters for Fe.

	c_1	c_2	μ
Fe	−0.26204	2.4483	3.3087
Fe^{1+}	0.01211	3.0288	3.8137
Fe^{2+}	0.32536	3.7736	4.3604
Fe^{3+}	0.39088	4.0404	4.6012
Fe^{4+}	0.42081	4.2388	4.8089
Fe^{5+}	0.42146	4.3842	4.9943
Fe^{6+}	0.39505	4.4850	5.1630
Fe^{7+}	0.34451	4.5541	5.3217
Fe^{8+}	0.26780	4.5881	5.4711
Fe^{9+}	0.18490	4.4630	5.6181
Fe^{10+}	0.10859	4.3020	5.7978
Fe^{11+}	0.07056	4.1180	6.0499
Fe^{12+}	0.12054	3.8923	6.4312
Fe^{13+}	0.45863	3.7928	7.1578
Fe^{14+}	1.5056	4.6481	8.6559
Fe^{15+}	−1.1759	0.0010	6.2583

Teble IV. Comparison of single electron energy eigenvalues for Ne (a.u.).

Ion	Shell	HS[a]	Present[b]
Ne	1s	31.493	31.335
	2s	1.584	1.555
	2p	0.735	0.734
Ne^{3+}	1s	34.795	34.706
	2s	4.154	4.125
	2p	3.339	3.331
Ne^{7+}	1s	41.276	41.276
	2s	8.819	8.812

[a] Herman Skillman method (Ref. 9).
[b] Model potential method.

Teble V. Comparison of single electron energy eigenvalues for Ti (a.u.).

Ion	Shell	HS[a]	Present[b]
Ti	1s	180.383	181.825
	2s	20.261	20.041
	2p	17.141	17.033
	3s	2.491	2.556
	3p	1.638	1.709
	3d	0.314	0.328
	4s	0.229	0.204
Ti^{10+}	1s	189.912	189.399
	2s	29.202	29.115
	2p	26.170	26.186
	3s	9.698	9.722

[a] Herman Skillman method (Ref. 9).
[b] Model potential method.

Teble VI. Comparison of K X-ray emission rates ($\times 10^{14}$ sec^{-1}).

	HS[a]		Present[b]	
Ion	2p→1s	3p→1s	2p→1s	3p→1s
Ti	2.539	0.288	2.612	0.298
Ti^{2+}	2.540	0.290	2.544	0.295
Ti^{4+}	2.538	0.322	2.539	0.323
Fe	5.385	0.648	5.547	0.675
Fe^{2+}	5.386	0.650	5.406	0.665
Fe^{8+}	5.392	0.841	5.396	0.837

[a] Herman Skillman method (Ref. 9).
[b] Model potential method.

overestimate the HS potential It is also clear that the present model potential is better approximation to the HS potential than the GSZ potential. This is probably ascribed to the fact that the present potential is obtained from the least-squares fit to the HS potential, while the d value in the GSZ potential is determened by adjusting the potential to the HF energies.

Tables II and III show the values for the parameters in Ti and Fe. As already seen for Ne, these values change continuously with increasing the degree of ionicity up to Ti^{10+} and Fe^{14+}. At ions Ti^{11+} and Fe^{15+}, there is a large discontinuity. These ions correspond to the Na-like Ti and Fe. Combining with the result for Ne, it can be said that the large change in the parameter values occurrs at the ion with closed shell plus one electron.

In order to test the model potential obtained in the present work, we have calculated the energy eigenvalues and the radiative transition probabilities for atoms and ions. Using the model potentials with the paramenters in the tables, the single-electron energy eigenvalues and wave functions for atomic orbitals with principal quantum number n and orbital quantum number l are obtained by solving the single-electron Schrödinger equation numerically.

Tables IV shows the comparion of the single-electron energy eigenvalues for various atomic orbitals, denoted by nl, in Ne atom and ions with those of the HS calculations. The similar comparison for Ti atom and ions is given in Table V. Agreement between the results of the model potential method and the HS eigenvalues is quite good.

The radiative transition probabilities in atoms and ions have been calculated in the dipole approximation.[12,13] The calculated $K\alpha(2p\rightarrow 1s)$ and $K\beta(3p\rightarrow 1s)$ X-ray emission rates are listed in Table VI and compared with the rates obtained by the HS wave functions. For neutral atoms, the present values are slightly larger than the HS values, but the discrepancy is less than 4%. In the case of ions, agreement is better.

4. CONCLUSION

We have calculated the model potentials for atoms and ions as an approximation to the SCF potential. The HFS calculation was performed to obtain the SCF potential. The numerical potential was fitted to an analytical function by the nonlinear least-squares method and the values of the parameters in the analytical function were determined. The obtained model potentials were used to calculate the energy eigenvalues and wave functions and tested by comparing the single-electron energy eigenvalues and the X-ray emission rates with those from the numerical HFS calculations. The results indicate that the present model potential is satisfactory to describe the energies and wave functions of electrons in atoms and ions.

In the present work, we used the HS program to obtain the SCF potentials in atoms and ions. However, the present method is quite general and we can apply this method to any type of potentials. In the case of the HS potential, the boundary conditions of the potential at small and large limits of r are given by Eqs. (2) and (3). When we use other potentials, these conditions may be changed and then the values of the constants, a and b, should be modified correspondingly. In this work, we used the polynomial up to $n=2$ in Eq. (1). It is also possible to use higher-order polynomials to obtain better approximation to the SCF potential.

ACKNOWLEGEMENTS

This work has been performed under the Japanese-Hungarian Cooperative Research

Program. The authors would like to express their thanks to the Japan Society for Promotion of Science (JSPS) and the Hungarian Academy of Sciences (MTA) for their financial support.

REFERENCES

(1) A. Hibbert, *Adv. At. Mol. Phys.*, **18**, 309 (1982).
(2) C. Laughlin and G.A. Victor, *Adv. At. Mol. Phys.*, **25**, 163 (1988).
(3) B.H. Bransden, A.M. Ermolaev, *Phys. Lett.*, **84A**, 316 (1981); A.M. Ermolaev, *J. Phys. B : At. Mol. Phys.*, **17**, 1069 (1984); A.M. Ermolaev and B.H. Bransden, *ibid.*, **17**, 1083 (1984); B.H Bransden, A.M. Ermolaev, and R Shingal, *ibid.*, **17**, 4515 (1984).
(4) W. Fritsch and C.D. Lin, *J. Phys. B : At. Mol. Phys.*, **17**, 3271 (1984).
(5) M.R.C. McDowell and R.K. Janev, *J. Phys. B : At. Mol. Phys.*, **18**, L295 (1985).
(6) K. Katsonis and G. Maynard, *J. de Phys. (Paris)*, **IV**, C1 313 (1991).
(7) A.E.S. Green, D.L. Sellin and A.S. Zachor, *Phys. Rev.*, **184**, 1 (1969); P.P Szydlik and A.E.S. Geen, *Phys. Rev. A*, **9**, 1885 (1974).
(8) R. Daniele, *J. Chem. Phys.*, **70**, 3462 (1979).
(9) F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice Hall, Engelwood Cliffs, NJ (1963).
(10) R. Latter, *Phys. Rev.*, **99**, 510 (1955).
(11) M.J.D. Powell, *Comput. J.*, **7**, 155 (1964).
(12) H.A Bethe and E.E. Salpeter, "Quantum Mechanics of One- and Two-Electron Systems," Springer, Berlin (1957).
(13) S.T. Manson and D.J. Kennedy, *At. Data Nucl. Data Tables*, **14**, 11 (1974).